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C4+ Surrogate Models for Thermophysical Properties of Aviation Kerosene RP-3 at Supercritical Pressures

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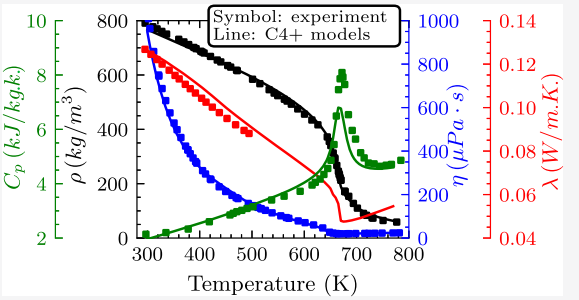
ABSTRACT: Due to the complexity of the chemical compositions in aviation kerosene, simplified surrogate models have gained significant attention to effectively reproduce the thermophysical properties of aviation kerosene. The available surrogate models usually adopt uniform representative compositions with a fixed ratio. However, given that aviation kerosene is an extremely complex mixture and associated with physicochemical reactions in actual heating processes, such simple models generally cannot accurately reproduce the thermophysical properties of aviation kerosene in a wide range of temperatures and pressures. Therefore, this work aims to develop accurate and independent surrogate models named C4+ for various thermophysical properties of aviation kerosene RP-3 at supercritical pressures. The thermophysical properties include density, viscosity, constant-pressure heat capacity, and thermal conductivity. The C4+ surrogate models are determined by using a carefully designed genetic algorithm to minimize the relative deviations between the calculated and experimental data of the corresponding properties based on the previous C4 surrogate model. Especially, the effects of pyrolysis and autoxidation reactions have been equivalently introduced to the corrections of the surrogate models. Consequently, the prediction of our surrogate models shows overall good agreement with the experimental measurements and the highest accuracy among all simplified surrogate models so far.



1. INTRODUCTION

Aviation kerosene often serves as a coolant in regenerative cooling systems before it is sent to the combustion chamber.[1−6] For scramjet applications, the pressures in the cooling channel generally range from 3 to 7 MPa, which are above the thermodynamic critical pressures of most aviation kerosene.[7] In the high-pressure region, the thermophysical properties of aviation kerosene are quite different from those at normal temperatures and pressures.[8,9] Accurately evaluating the thermophysical properties of aviation kerosene at supercritical pressures is of great importance and a prerequisite for further analysis of kerosene-related heat transfer processes and development of thermal management techniques in aircraft engines.

Since aviation kerosene is a very complex mixture consisting of hundreds of compounds, including alkanes, cycloalkanes, arenes, and so forth,[10] it is a big challenge to identify all compositions and may be more difficult to directly calculate the thermophysical properties of such complex mixtures. Therefore, experiments are the most straightforward and reliable way to get the thermophysical properties of aviation kerosene. However, first, due to the difficulty and high cost of measurements at supercritical pressures, the current experimental data of aviation kerosene RP-3 are very limited. Moreover, the thermophysical properties of supercritical fluids are extremely sensitive to the temperature and pressure.[9] The sparse and discrete data will result in errors in the interpolation of the thermophysical properties in the region where the experimental data are still unavailable. Therefore, the theoretical or numerical predictions still play an important role in probing the thermophysical properties of aviation kerosene. To enable the prediction of complex aviation kerosene, much effort has been devoted to the development of a surrogate model, which consists of only a few well-defined simple compounds and yet possesses similar thermophysical properties to those of aviation kerosene. Once a surrogate model is determined, it is ready to evaluate the thermophysical properties of the newly generated and simplified mixtures by the extended corresponding-states principle (CSP)[11] or molecular dynamics simulations.[12−15] The outputs could serve as the effective approximations of the thermophysical properties of aviation kerosene. All prominent advantages make surrogate models the most attractive and popular way to predict the thermophysical properties of aviation kerosene.

Table 1 lists several typical surrogate models and their performance on the prediction of several fundamental

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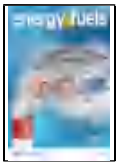

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Table 1. Average and Maximum Relative Deviations of Different Thermophysical Properties of Aviation Kerosene RP-3 between Experimental and Calculated Data of Typical Surrogate Models

				ρ		η		C_p		λ		
ID	author	year	number of components	max (%)[a]	ave (%)[b]	max (%)	ave (%)	max (%)	ave (%)	max (%)	ave (%)	T_{pc}[c]
(1)	Mawid et al.[16]	2003	4	108.86	12.85	115.53	23.51	31.68	14.62	13.36	10.56	√
(2)	Fan and Yu[17]	2006	3	70.42	10.50	47.92	10.46	56.05	13.40	3.36	1.68	↓
(3)	Zhong et al.[7]	2009	10	141.87	21.01	176.73	40.28	49.55	14.27	18.19	14.88	↑
(4)	Pei and Hou[18]	2017	4	123.77	23.34	136.81	28.95	31.12	13.47	11.46	7.99	√
(5)	Yu and Gou[19]	2018	3	91.02	11.71	29.03	7.99	46.75	12.51	10.03	7.33	↓
(6)	Yi et al.[20]	2019	4	92.55	8.34	66.57	17.31	46.18	14.42	8.18	5.57	↓
(7)	Liu et al.[21]	2020	5	109.04	12.00	77.56	31.12	41.91	13.39	5.57	3.46	↓
(8)	Shen et al.	this work	4 + 2	14.83	3.31	9.06	3.35	20.07	3.33	6.88	4.41	√

[a]Maximum relative deviation. [b]Average relative deviation. [c]Pseudo-critical temperature, √, ↑, and ↓ refer to accurate estimate, overestimate, and underestimate, respectively.

thermophysical properties of aviation kerosene RP-3. For density (ρ), viscosity (η), and constant-pressure heat capacity (C_p), the related temperature and pressure of data analysis are up to 770 K and 5 MPa, respectively, while for thermal conductivity (λ), the related temperature is only up to 500 K due to the lack of experimental data. It can be concluded that there is still no single surrogate model able to accurately reproduce the various thermophysical properties of aviation kerosene RP-3 at supercritical pressures to date. Two significant factors may have led to this failure. One is that a single surrogate model is insufficient to capture the sharp changes of the various properties of aviation kerosene. The other is that the effects of some physicochemical reactions such as pyrolysis and autoxidation cannot be reflected in a single surrogate model with a fixed composition. Indeed, the relative deviations between the calculated and experimental results of different properties increase drastically as the fluid temperature rises above a threshold temperature (e.g., 700 K) at all different supercritical pressures. Therefore, there is an urgent need for reliable and accurate surrogate models of aviation kerosene RP-3 which could supply sufficient thermophysical data in a wide temperature and pressure range.

In this work, we develop new surrogate models named C4+ aiming to accurately predict the thermophysical properties of aviation kerosene RP-3 including density, viscosity, constant-pressure heat capacity, and thermal conductivity at supercritical pressures with temperatures up to 770 K. In Section 2, we illustrate how the C4+ surrogate models are generated in detail and briefly introduce the theoretical backgrounds of the extended CSP and the genetic algorithm (GA). In Section 3, we evaluate the accuracy of our C4+ surrogate models by comparing with the available experimental measurements and the previous surrogate models. The main conclusions of this study are summarized in Section 4.

2. METHODOLOGY

2.1. Formulation of C4+ Surrogate Models. Since in the research of heat transfer or spray characteristics of aviation kerosene, the major concern is to predict the thermophysical properties accurately with little reaction mechanism considered, our focus is put on how to improve the surrogate models to reproduce these data with experimental accuracy. Previous surrogate models were developed mostly based on the composition or functional group similarity with that of the real aviation kerosene. These surrogate models could roughly approximate multiple properties of aviation kerosene at the cost of accuracy or flexibility, whereas developing an individual surrogate model for a unitary property possesses high flexibility and holds great potential to yield the highest accuracy. After different thermophysical properties are calculated, they could be combined into a complete database and applied in the analysis of fluid flow and heat transfer of aviation kerosene. Therefore, we propose different surrogate models for different thermophysical properties of aviation kerosene RP-3. The properties considered in this work are density, viscosity, constant-pressure heat capacity, and thermal conductivity.

To build a surrogate model of aviation kerosene, the first and critical ingredient is to pick several suitable representatives of the chemical compositions. A previous study[11] has shown that the C4 surrogate model[16] consisting of n-decane, n-dodecane, methylcyclohexane, and n-butylbenzene exhibits relatively high reliability in predicting various thermophysical properties of the aviation kerosene RP-3 at supercritical pressures. Therefore, we adopt the same compositions in our surrogate models as those of the C4 surrogate model. The mole fractions of the surrogate model for different properties are separately determined by using the deterministic crowding (DC) GA to minimize the relative deviations between the predicted values and experimental values.

Moreover, to further improve the precision of the surrogate models, we take the effects of pyrolysis and autoxidation reactions[22] into account. Pyrolytic reactions usually occur at a relatively high temperature (i.e., $T \geq 670$ K), which would lead to the change of chemical compositions in kerosene. Autoxidation is a process where aviation kerosene interacts with dissolved oxygen at about $T \leq 530$ K. The autoxidation process will not change the compositions of the fuel significantly, though it would have a remarkable impact on the heat capacity due to endothermic effects.[18] Concerning the effects of these two reaction processes, we propose further corrections on the optimized surrogate models to reduce the deviation between the calculated and experimental data, as shown in Figure 1. For density and viscosity, new additional components are introduced to the optimized surrogate models (cyclopentane for the density surrogate model and n-octadecane for the viscosity surrogate model) in the high-temperature range to represent the composition changes caused by pyrolysis. The new components are not the real cracked products but represent the effects of pyrolysis on the thermophysical properties. The mole fractions of the newly introduced components are set to a function of temperature and pressure. The function is fitted with the best mole fraction of the new component at (T, P), which minimizes the deviation between the calculated and experimental data at this

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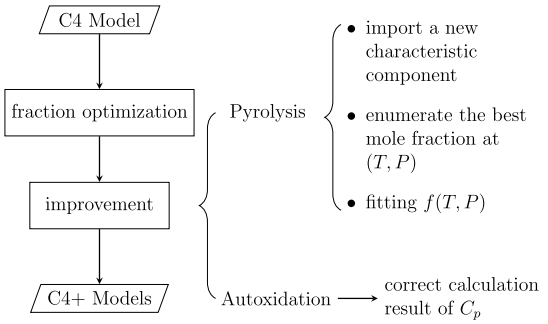

Figure 1. Schematic diagram of the construction of C4+ surrogate models.

point. With different components added, the linearity of the function would be different, and so would be the relative deviations between the model-predicted and experimental data. By comparing a dozen species, we finally choose cyclopentane and n-octadecane since they show the best performance among various substances. Since heat capacity is influenced by those two chemical reactions remarkably, instead of introducing new components, we apply a numerical correction on the calculated results to reflect the effect of the two processes simultaneously. Due to the lack of experimental data at high temperatures, no further correction for thermal conductivity is taken. When more data are available, similar procedures can be used to optimize the model.

2.2. Extended Corresponding-States Principle. The CSP[23] is a theorem that reveals the similarity of different fluids. According to the CSP theory, if two fluids are conformal, the following equation exists

$$a_x^r(\rho_x, T_x) = a_0(\rho_x h_{x,0}, T_x f_{x,0}) \tag{1}$$

where a is the residual Helmholtz free energy, T is the absolute temperature, and ρ is the fluid density. The subscripts x and 0 refer to the fluid of interest and the reference fluid, respectively. The scale factors $h_{x,0}$ and $f_{x,0}$ are called the equivalent substance-reducing ratios and are functions of the critical parameters of the two fluids

$$h_{x,0} = \frac{\rho_0^c}{\rho_x^c}, f_{x,0} = \frac{T_x^c}{T_0^c} \tag{2}$$

where the superscript c indicates a critical point value. Based on this relation, the thermodynamic properties of the unknown fluid can be calculated with the reference fluid whose properties are already known. However, only spherical and symmetric molecules satisfy this relation strictly, and for most real fluids, this formula is no longer applicable. Therefore, in the extended CSP, two shape factors $\theta_{x,0}$ and $\phi_{x,0}$ are introduced in the scale factors to reflect the effects of the molecule polarity

$$f_{x,0} = (T_x^c/T_0^c)\theta_{x,0}(T_x^*, V_x^*, \omega_x)$$
$$h_{x,0} = (\rho_0^c/\rho_x^c)\phi_{x,0}(T_x^*, V_x^*, \omega_x) \tag{3}$$

where V is the specific volume and the asterisk indicates reduction by the critical point value. $\theta_{x,0}$ and $\phi_{x,0}$ are functions of the acentric factor ω and of the reduced variables T_x^* and V_x^*. In the case of mixtures, an equivalent hypothetical pure fluid can be used for calculation whose scale factors are defined as

$$h_{x,0} = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j h_{i,j} \tag{4}$$

and

$$f_{x,0}h_{x,0} = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j f_{i,j} h_{i,j} \tag{5}$$

by the van der Waals mixing rules. In the equations, x_i is the concentration of the component i in the mixture, and the cross terms are given as

$$f_{ij} = \sqrt{f_i f_j}(1 - k_{ij}) \tag{6}$$

and

$$h_{ij} = (h_i^{1/3} + h_j^{1/3})^3(1 - l_{ij})/8 \tag{7}$$

where k_{ij} and $l_{i,j}$ are binary interaction parameters. For more details about the extended CSP, the reader can refer to refs 24 and 25.

For transport property calculations including viscosity and thermal conductivity calculations, the model based on the extended CSP proposed by Ely and Hanley[26,27] is widely used. In this model, the transport property (i.e., viscosity) of an unknown fluid can be calculated with the reference fluid as

$$\eta_x(\rho, T) = \eta_0(\rho_{x,0}h_{x,0}, T_{x,0}/f_{x,0})F_\eta \tag{8}$$

where

$$F_\eta = \left(\frac{M_x}{M_0}\right)^{1/2} f_{x,0}^{1/2} h_{x,0}^{-2/3} \tag{9}$$

where M is the molecular weight. The viscosity of the reference fluid can be calculated by the empirical expression

$$\eta_0(\rho_0, T_0) = \eta_0^{(1)}(T_0) + \eta_0^{(2)}(T_0)\rho_0 + \Delta\eta_0(\rho_0, T_0)X_\eta \tag{10}$$

where $\eta_0^{(1)}$ represents the dilute gas viscosity, $\eta_0^{(2)}$ is the first density correction, and $\Delta\eta_0$ dominates the viscosity correction at high density. More details concerning transport property calculations can be found in refs 26 and 27.

The extended corresponding-states method for calculating thermophysical properties of hydrocarbon fuels at supercritical pressures is widely adopted, and its effectiveness has been validated in many studies.[28−31] In this article, the SUPERTRAPP program,[32] which integrates the extended corresponding-states methods and the hydrocarbon database, is used to calculate thermodynamic and transport properties of the surrogate models.

2.3. Genetic Algorithm. The GA[33] is a heuristic optimization method imitating the process of evolution wherein a set of solutions evolves over a sequence of generations. During the evolution, good solutions are selected and bad solutions are eliminated according to the fitness. Meanwhile, in each generation, new solutions are generated from the good ones by cross-over and mutation operations to explore the new solution space. After a sequence of iterations, the population gradually converges to an optimal solution. Since the GA was proposed, much research has been done to improve the performance of the algorithm, resulting in algorithms such as the niching algorithm,[34] parallel recombi-

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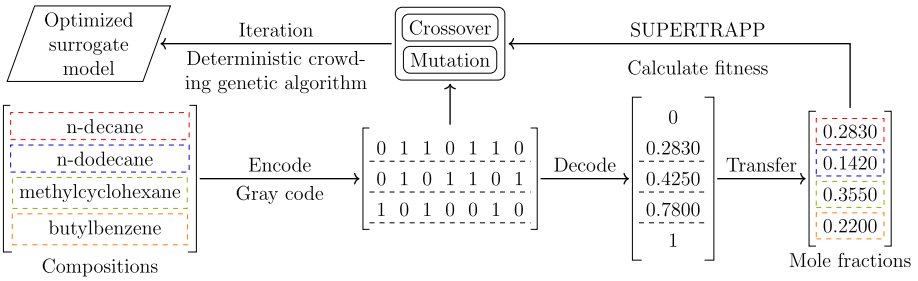

Figure 2. Schematic diagram of the optimization of surrogate models.

native simulated annealing algorithm,[35] and adaptive GA.[36] In this work, we adopt the DC algorithm[37] to perform the optimization of the surrogate models because the previous research shows that DC is generally good for problems of all levels of complexity.[38] DC compares the similarity between individuals, makes competition between similar ones, and eliminates the ones with less fitness to maintain the diversity of the population. More details about the DC algorithm can be found in ref 37.

The main procedure of the optimization is shown in Figure 2. The mole fractions of a surrogate model with four species can be represented by three float point numbers, which stand for three break points in (0, 1). Here, we use gray code to encode each surrogate model to enhance the local search capability of the algorithm.[39] After the gray codes are decoded and further transferred to the mole fractions, the SUPERTRAPP program is called to calculate the thermophysical properties of the surrogate model. The fitness is defined as the reciprocal of the sum of the relative deviations between the calculated and experimental data at various temperatures and pressures. The experimental data of aviation kerosene RP-3 is from refs 40−43. Based on the fitness, the solutions can evolve by the rules defined in the DC algorithm. After several iterations, the solutions converge to an optimal surrogate model.

3. RESULTS AND DISCUSSION

In this section, we present the detailed forms of the C4+ surrogate models for density, viscosity, constant-pressure heat capacity, and thermal conductivity of aviation kerosene RP-3. In addition, we evaluate the accuracy of the C4+ surrogate models compared with the previous C4 surrogate model and experimental data.

3.1. Density.

Table 2 shows the optimized specific compositions and their corresponding mole fractions in the C4 and C4+ surrogate models for density. In the optimized surrogate model, n-decane occupies the most proportion and methylcyclohexane vanishes. It indicates that a simple surrogate model consisting of n-decane is also an acceptable option for aviation kerosene RP-3, which is in accordance with the results reported by ref 11. Also, a lighter component, cyclopentane, is added to our C4+ surrogate model to reduce the deviation between the calculated and experimental density in the relatively high temperature region where the pyrolysis reaction is more possible to happen. We find that within the experimental temperature and pressure ranges, the optimized mole fraction of cyclopentane increases approximately linearly with the temperature at different supercritical pressures. Therefore, the mole fraction of cyclopentane in the C4+ surrogate model for density is

$$f(T) = \max(0.00767T - 5.29,\ 0) \tag{11}$$

which is a linear function of temperature. The minimum of f(T) is 0, and in this case, the C4+ surrogate model for density is just the optimized surrogate model with the fixed ratio.

Table 2. Comparisons of Compositions between the C4+ Surrogate Model for Density and the C4 Surrogate Model

species	chemical formula	mole fractions	
		C4	C4+ (ρ)
n-decane	$C_{10}H_{22}$	0.2030	0.6220 × (1 − f(T))[a]
n-dodecane	$C_{12}H_{26}$	0.3810	0.1100 × (1 − f(T))
methylcyclohexane	C_7H_{14}	0.1470	0
n-butylbenzene	$C_{10}H_{14}$	0.2690	0.2680 × (1 − f(T))
cyclopentane	C_5H_{10}	0	f(T)

[a]f(T) = max(0.00767T − 5.29,0), T: temperature (K).

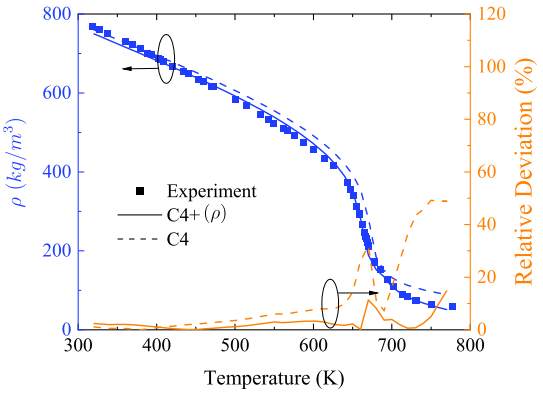

Figure 3. Comparisons of densities calculated using the C4+ surrogate model and the C4 surrogate model with experimental data of aviation kerosene RP-3 at 3 MPa.

Figure 3 shows the density at 3 MPa calculated by the two surrogate models and measured by experiments. The experimental results are derived from ref 40. The relative deviations between the surrogate models and the experiments are also illustrated. It is indicated that the relative deviation of the C4 surrogate model increases as the temperature increases. The reliability of the C4 surrogate model sharply declines in the region of T ≥ 690 K, whereas our surrogate model exhibits a better prediction in the high temperatures. This is good evidence for the necessity of the correction.

Table 3 lists the relative deviations between the model-calculated and experimental densities at various supercritical pressures. It more clearly shows that the prediction accuracy of our surrogate model has a significant improvement in

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Table 3. Average and Maximum Relative Deviations of Density of Aviation Kerosene RP-3 between Calculated and Experimental Data at Various Supercritical Pressures

	3 MPa		4 MPa		5 MPa	
surrogate model	ave (%)	max (%)	ave (%)	max (%)	ave (%)	max (%)
C4	11.43	49.22	17.56	108.06	10.73	99.25
C4+	2.66	14.83	3.21	14.33	4.07	13.77

comparison with that of the C4 surrogate model. The average relative deviation of the original C4 surrogate model is larger than 10%, and the maximum relative deviation is larger than 108%, whereas the average relative deviation of the newly developed surrogate model is less than 5%, and the largest relative deviation is only 14.83%. The improvement of accuracy comes from both the optimization and the correction in high-temperature ranges.

3.2. Viscosity. The optimized mole fractions of the C4+ viscosity surrogate model are shown in Table 4. Likewise, after optimization, n-decane occupies the highest proportion and the mole fraction of n-butylbenzene tends to 0. n-Octadecane is introduced to improve the C4+ surrogate model for predicting the viscosity of aviation kerosene RP-3 at high temperatures. Within the experimental ranges, the best mole fraction of n-octadecane shows a linear dependence with both temperature and pressure. Therefore, the mole fraction of n-octadecane in the C4+ surrogate model for viscosity is

Table 4. Comparisons of Compositions between the C4+ Surrogate Model for Viscosity and the C4 Surrogate Model

		mole fractions	
species	chemical formula	C4	C4+ (η)
n-decane	$C_{10}H_{22}$	0.2030	0.6320 × (1 − g(T,P))[a]
n-dodecane	$C_{12}H_{26}$	0.3810	0.1520 × (1 − g(T,P))
methylcyclohexane	C_7H_{14}	0.1470	0.2160 × (1 − g(T,P))
n-butylbenzene	$C_{10}H_{14}$	0.2690	0
n-octadecane	$C_{18}H_{38}$	0	g(T, P)

[a]g(T,P) = max(0.0054T − 0.19P − 2.97,0); T: temperature (K) and P: pressure (MPa).

$$g(T, P) = \max(0.0054T - 0.19P - 2.97, 0) \quad (12)$$

which is a linear function of both temperature and pressure. The minimum of g(T,P) is 0, and in this case, the C4+ surrogate model for viscosity is just the optimized surrogate model with the fixed ratio.

Figure 4 shows the model-predicted and experimental viscosities of aviation kerosene RP-3 at 3 MPa. The relative deviations between surrogate models and experiments are also calculated. The experimental results are derived from ref 41. The results indicate that the performance of our surrogate model is remarkably high. Especially, our model can accurately predict the transition of viscosity in the trans-critical region. In addition, due to the corrections, our surrogate model still maintains high performance in the high-temperature range.

The detailed deviation analyses of viscosity at various pressures are provided in Table 5. The average relative deviation of the original C4 surrogate model is larger than 20%, and the maximum relative deviation is over 110% at 3 MPa, whereas the average and maximum relative deviations of our surrogate model are less than 4% and 10%, respectively. The results indicate that our model can well reproduce the viscosity of aviation kerosene RP-3.

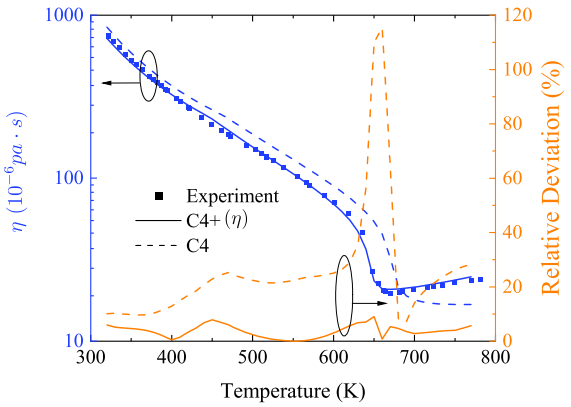

Figure 4. Comparisons of viscosities calculated using the C4+ surrogate model and the C4 surrogate model with experimental data of aviation kerosene RP-3 at 3 MPa.

Table 5. Average and Maximum Relative Deviations of Viscosity of Aviation Kerosene RP-3 between Calculated and Experimental Data at Various Supercritical Pressures

	3 MPa		4 MPa		5 MPa	
surrogate model	ave (%)	max (%)	ave (%)	max (%)	ave (%)	max (%)
C4	25.44	115.54	23.74	56.66	21.35	45.90
C4+	3.70	9.06	3.23	7.46	3.11	7.41

3.3. Constant-Pressure Heat Capacity. Table 6 shows the optimized mole fractions of the surrogate model for constant-pressure heat capacity. It can be noted that the mole fraction of n-butylbenzene becomes 0 and n-decane still takes up the highest proportion. However, due to autoxidation and pyrolysis processes, the calculated heat capacity of the optimized surrogate model is still lower than that of the experiments. To improve the performance of the surrogate model, we find that at any supercritical pressure, the ratio between the calculated and experimental heat capacities increases approximately linearly with the temperature. Therefore, a correction factor

Table 6. Comparisons of Compositions between the C4+ Surrogate Model for Constant-Pressure Heat Capacity and the C4 Surrogate Model

		mole fractions	
species	chemical formula	C4	C4+ (C_p)[a]
n-decane	$C_{10}H_{22}$	0.2030	0.6850
n-dodecane	$C_{12}H_{26}$	0.3810	0.2913
methylcyclohexane	C_7H_{14}	0.1470	0.0237
n-butylbenzene	$C_{10}H_{14}$	0.2690	0

[a]Multiply calculated results by R, R = 7.78 × 10^{-4}T + 0.7104.

$$R = 7.78 \times 10^{-4}T + 0.7104 \quad (13)$$

is calculated by linear fitting. The final calculated result of the C4+ surrogate model for constant-pressure heat capacity is the product of R and the value calculated by the optimized surrogate model.

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Figure 5 shows the constant-pressure heat capacity at 3.02 MPa calculated by the two surrogate models and measured by

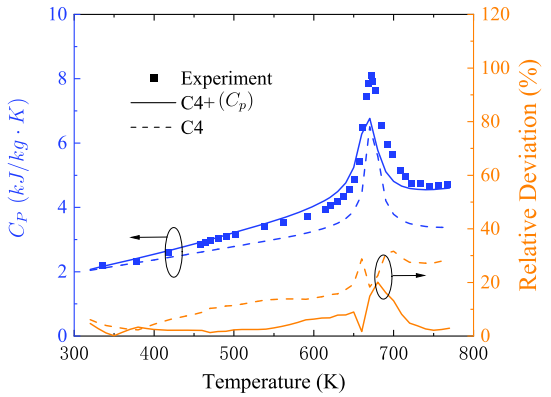

Figure 5. Comparisons of constant-pressure heat capacities calculated using the C4+ surrogate model and the C4 surrogate model with experimental data of aviation kerosene RP-3 at 3.02 MPa.

experiments. The experimental results are derived from ref 42. The relative deviations between the surrogate models and the experiments are also illustrated. It can be seen that the relative deviation of the C4 surrogate model increases as the temperature increases, whereas due to the corrections, our surrogate model maintains good performance in the whole temperature range.

Table 7 lists the relative deviations between the model-calculated and experimental constant-pressure heat capacities at various supercritical pressures. The results show that the prediction accuracy of our surrogate model has a significant improvement in comparison with that of the C4 surrogate model. The average and maximum relative deviations of the C4 surrogate model are larger than 14% and 30%, respectively, whereas the average relative deviation of the newly developed surrogate model is less than 5%, and the largest relative deviation 20.34% occurs in the trans-critical region at 3.02 MPa due to the sharp change of the heat capacity.

3.4. Thermal Conductivity. Since only experimental data with the temperature less than 500 K for thermal conductivity of aviation kerosene RP-3 are available, the surrogate model is optimized without further corrections. To maintain the ability of the surrogate model to predict the pseudo-critical temperature with the lack of experimental data, we set the fitness to zero in the optimization if the surrogate model cannot capture the pseudo-critical temperature at any supercritical pressure. The optimized mole fractions of the C4+ surrogate model for thermal conductivity are shown in Table 8. n-Butylbenzene occupies more than 80% proportion in the new surrogate model, and the mole fractions of n-dodecane and methylcyclohexane become 0. It is noteworthy that the optimized mole fractions for thermal conductivity are quite

Table 8. Comparisons of Compositions between the C4+ Surrogate Model for Thermal Conductivity and the C4 Surrogate Model

species	chemical formula	mole fractions	
		C4	C4+ (λ)
n-decane	$C_{10}H_{22}$	0.2030	0.1430
n-dodecane	$C_{12}H_{26}$	0.3810	0
methylcyclohexane	C_7H_{14}	0.1470	0
n-butylbenzene	$C_{10}H_{14}$	0.2690	0.8570

different from those of other properties, which may be due to the insufficient experimental data.

Figure 6 shows the model-predicted and experimental thermal conductivities of aviation kerosene RP-3 at 3 MPa.

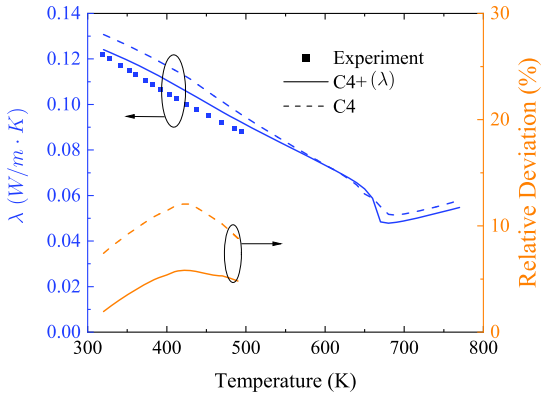

Figure 6. Comparisons of thermal conductivities calculated using the C4+ model and the C4 model with experimental data of aviation kerosene RP-3 at 3 MPa.

The relative deviations between surrogate models and experiments are also calculated. The experimental results are derived from ref 43. Results show that the performance of the newly developed surrogate model is well-improved. In the meantime, our surrogate model can still predict the pseudo-critical temperature accurately.

The detailed deviation analyses of thermal conductivity at various supercritical pressures are provided in Table 9 with the

Table 9. Average and Maximum Relative Deviations of Thermal Conductivity of Aviation Kerosene RP-3 between Calculated and Experimental Data at Various Supercritical Pressures

surrogate model	3 MPa		4 MPa		5 MPa	
	ave (%)	max (%)	ave (%)	max (%)	ave (%)	max (%)
C4	9.94	12.06	10.05	12.65	10.65	13.34
C4+	4.21	5.80	4.26	6.29	4.76	6.88

Table 7. Average and Maximum Relative Deviations of Constant-Pressure Heat Capacity of Aviation Kerosene RP-3 between Calculated and Experimental Data at Various Supercritical Pressures

surrogate model	3.02 MPa		4.02 MPa		4.98 MPa		5.98 MPa	
	ave (%)	max (%)	ave (%)	max (%)	ave (%)	max (%)	ave (%)	max (%)
C4	14.38	31.86	14.00	27.96	15.06	28.40	14.86	28.89
C4+	4.61	20.07	2.35	10.24	4.70	2.24	1.65	5.81

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Table 10. Comparison between the Compositions of C4+ Surrogate Models and That of the C4 Surrogate Model

		surrogate model components in mole fractions				
			C4+			
species	chemical formula	C4	ρ	η	C_p[a]	λ
n-decane	$C_{10}H_{22}$	0.2030	0.6220 × (1 − f(T))[b]	0.6320 × (1 − g(T, P))[c]	0.6850	0.1430
n-dodecane	$C_{12}H_{26}$	0.3810	0.1100 × (1 − f(T))	0.1520 × (1 − g(T, P))	0.2913	0
methylcyclohexane	C_7H_{14}	0.1470	0	0.2160 × (1 − g(T, P))	0.0237	0
n-butylbenzene	$C_{10}H_{14}$	0.2690	0.2680 × (1 − f(T))	0	0	0.8570
cyclopentane	$C5H_{10}$	0	f(T)	0	0	0
n-octadecane	$C_{18}H_{38}$	0	0	g(T, P)	0	0

[a]Multiply calculated data by (7.78 × 10^{-4}T + 0.7104). [b]f(T) = max(0.00767T − 5.29,0). [c]g(T,P) = max(0.0054T − 0.19P − 2.97,0); T: temperature (K) and P: pressure (MPa).

temperature up to 500 K. At supercritical pressures, the average relative deviation between the calculated results from the C4 surrogate model and experimental data is larger than 9%, and the maximum deviation is larger than 12%, whereas for our surrogate model, the relative deviation is within 5% and the maximum deviation is less than 7%. Nevertheless, the prediction accuracy at high temperatures should be further verified when the experimental data are available in the future.

4. CONCLUSIONS

In this article, new surrogate models named C4+ are developed to predict four important thermophysical properties of aviation kerosene RP-3 at supercritical pressures including density, viscosity, constant-pressure heat capacity, and thermal conductivity. The detailed forms of C4+ surrogate models are summarized in Table 10. Basic components of C4+ surrogate models include n-decane, n-dodecane, methylcyclohexane, and n-butylbenzene. Then, the mole fractions of the four species are optimized based on the relative deviations between the calculated and experimental data of the targeted property. Finally, the effects of pyrolysis and autoxidation reactions have been equivalently introduced to the corrections of the surrogate models. For density and viscosity surrogate models, new components, that is, cyclopentane and n-octadecane, are introduced to the optimized models to reflect the effects caused by pyrolysis; for the constant-pressure heat capacity surrogate model, a correction function is applied to the calculated data to reflect pyrolysis and autoxidation processes simultaneously; and for the thermal conductivity surrogate model, because of the current limitation of experimental data, only the optimization is conducted. The comparison between the calculated and experimental data shows that C4+ surrogate models can accurately predict the four thermophysical properties of aviation kerosene RP-3 at various supercritical pressures.

■ ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.energyfuels.1c00326.

Calculated density, constant-pressure heat capacity, viscosity, and thermal conductivity using C4+ surrogate models (in .txt format) (ZIP)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Dang, G.; Zhong, F.; Zhang, Y.; Zhang, X. Numerical study of heat transfer deterioration of turbulent supercritical kerosene flow in heated circular tube. Int. J. Heat Mass Transfer 2015, 85, 1003−1011.

(2) Zhu, J.; Tao, Z.; Deng, H.; Wang, K.; Yu, X. Numerical investigation of heat transfer characteristics and flow resistance of kerosene RP-3 under supercritical pressure. Int. J. Heat Mass Transfer 2015, 91, 330−341.

(3) Feng, Y.; Qin, J.; Zhang, S.; Bao, W.; Cao, Y.; Huang, H. Modeling and analysis of heat and mass transfers of supercritical hydrocarbon fuel with pyrolysis in mini-channel. Int. J. Heat Mass Transfer 2015, 91, 520−531.

(4) Zhang, C.; Xu, G.; Gao, L.; Tao, Z.; Deng, H.; Zhu, K. Experimental investigation on heat transfer of a specific fuel (RP-3) flows through downward tubes at supercritical pressure. J. Supercrit. Fluids 2012, 72, 90−99.

(5) Zhu, J.; Tao, K.; Tao, Z.; Qiu, L. Heat transfer degradation of buoyancy involved convective RP-3 hydrocarbon fuel in vertical tubes with various diameters under supercritical pressure. Appl. Therm. Eng. 2019, 163, 114392.

(6) Tao, Z.; Li, L.; Zhu, J.; HU, X.; WANG, L.; Qiu, L. Numerical investigation on flow and heat transfer characteristics of supercritical RP-3 in inclined pipe. Chin. J. Aeronaut. 2019, 32, 1885−1894.

(7) Zhong, F.; Fan, X.; Yu, G.; Li, J.; Sung, C.-J. Heat transfer of aviation kerosene at supercritical conditions. J. Thermophys. Heat Transfer 2009, 23, 543−550.

(8) Hendricks, R. C.; Simoneau, R. J.; Smith, R. V. Advances in Cryogenic Engineering; Springer, 1995; pp 197−237.
(9) Pioro, I.; Mokry, S.; Draper, S. Specifics of thermophysical properties and forced-convective heat transfer at critical and supercritical pressures. Rev. Chem. Eng. 2011, 27, 191−214.
(10) Dagaut, P.; Cathonnet, M. The ignition, oxidation, and combustion of kerosene: A review of experimental and kinetic modeling. Prog. Energy Combust. Sci. 2006, 32, 48−92.
(11) Xu, K.; Meng, H. Analyses of surrogate models for calculating thermophysical properties of aviation kerosene RP-3 at supercritical pressures. Sci. China: Technol. Sci. 2015, 58, 510−518.
(12) Yang, X.; Duan, C.; Xu, J.; Liu, Y.; Cao, B. A numerical study on the thermal conductivity of H2O/CO2/H2 mixtures in supercritical regions of water for coal supercritical water gasification system. Int. J. Heat Mass Transfer 2019, 135, 413−424.
(13) Yang, X.; Feng, Y.; Jin, J.; Liu, Y.; Cao, B. Molecular dynamics simulation and theoretical study on heat capacities of supercritical H2O/CO2 mixtures. J. Mol. Liq. 2020, 299, 112133.
(14) Liu, Y.; Cao, B. Thermodynamic models for H2O-CO2-H2 mixtures in near-critical and supercritical regions of water. Int. J. Hydrogen Energy 2020, 45, 4297−4304.
(15) Han, S.; Li, X.; Guo, L.; Sun, H.; Zheng, M.; Ge, W. Refining Fuel Composition of RP-3 Chemical Surrogate Models by Reactive Molecular Dynamics and Machine Learning. Energy Fuels 2020, 34, 11381−11394.
(16) Mawid, M. A.; Park, T. W.; Sekar, B.; Arana, C. A. Development of Detailed Chemical Kinetic Mechanisms for Ignition/Oxidation of JP-8/Jet-A/JP-7 Fuels. Proceedings of ASME Turbo Expo, 2003; pp 1−12.
(17) Fan, X. J.; Yu, G. Analysis of thermophysical properties of Daqing RP-3 aviation kerosene. J. Propul. Technol. 2006, 27, 187.
(18) Pei, X. Y.; Hou, L. Y. Effect of different species on physical properties for the surrogate of aviation fuel. J. Tsinghua Univ., Sci. Technol. 2017, 57, 774−779.
(19) Yu, J.; Gou, X. Comprehensive surrogate for emulating physical and kinetic properties of jet fuels. J. Propul. Power 2018, 34, 679−689.
(20) Yi, R.; Chen, X.; Chen, C. P. Surrogate for emulating physicochemical and kinetics characteristics of RP-3 aviation fuel. Energy Fuels 2019, 33, 2872−2879.
(21) Liu, J.; Hu, E.; Zeng, W.; Zheng, W. A new surrogate fuel for emulating the physical and chemical properties of RP-3 kerosene. Fuel 2020, 259, 116210.
(22) Roan, M. A.; Boehman, A. L. The effect of fuel composition and dissolved oxygen on deposit formation from potential JP-900 basestocks. Energy Fuels 2004, 18, 835−843.
(23) Leland, T. W.; Chappelear, P. S. The Corresponding States Principle-a Review of Current Theory and Practice. Ind. Eng. Chem. 1968, 60, 15−43.
(24) Huber, M. L.; Ely, J. F. A predictive extended corresponding states model for pure and mixed refrigerants including an equation of state for R134a. Int. J. Refrig. 1994, 17, 18−31.
(25) Fisher, G. D.; Leland, T. W. Corresponding States Principle Using Shape Factors. Ind. Eng. Chem. Fundam. 1970, 9, 537−544.
(26) Ely, J. F.; Hanley, H. J. M. Prediction of transport properties. 1. Viscosity of fluids and mixtures. Ind. Eng. Chem. Fundam. 1981, 20, 323−332.
(27) Ely, J. F.; Hanley, H. J. M. Prediction of Transport Properties. 2. Thermal Conductivity of Pure Fluids and Mixtures. Ind. Eng. Chem. Fundam. 1983, 22, 90−97.
(28) Jiang, R.; Liu, G.; Zhang, X. Thermal cracking of hydrocarbon aviation fuels in regenerative cooling microchannels. Energy Fuels 2013, 27, 2563−2577.
(29) Yang, V. Modeling of supercritical vaporization, mixing, and combustion processes in liquid-fueled propulsion systems. Proc. Combust. Inst. 2000, 28, 925−942.
(30) Li, W.; Huang, D.; Xu, G.-q.; Tao, Z.; Wu, Z.; Zhu, H.-t. Heat transfer to aviation kerosene flowing upward in smooth tubes at supercritical pressures. Int. J. Heat Mass Transfer 2015, 85, 1084−1094.
(31) Huang, D.; Wu, Z.; Sunden, B.; Li, W. A brief review on convection heat transfer of fluids at supercritical pressures in tubes and the recent progress. Appl. Energy 2016, 162, 494−505.
(32) Huber, M. L. NIST Thermophysical Properties of Hydrocarbon Mixtures Database (SUPERTRAPP), Version 3.2; National Institute of Standards and Technology Standard Reference Data Program: Gaithersburg, MD 20899, 2007.
(33) Srinivas, M.; Patnaik, L. M. Genetic algorithms: A survey. computer 1994, 27, 17−26.
(34) Sareni, B.; Krahenbuhl, L. Fitness sharing and niching methods revisited. IEEE Trans. Evol. Comput. 1998, 2, 97−106.
(35) Adler, D. Genetic algorithms and simulated annealing: A marriage proposal. IEEE International Conference on Neural Networks, 1993; pp 1104−1109.
(36) Srinivas, M.; Patnaik, L. M. Adaptive probabilities of crossover and mutation in genetic algorithms. IEEE Trans. Syst. Man Cybern. 1994, 24, 656−667.
(37) De Jong, K. A. Analysis of the Behavior of a Class of Genetic Adaptive Systems; University of Michigan: USA, 1975; pp 233−236.
(38) Mahfoud, S. W. A. Comparison of Parallel and Sequential Niching Methods. Proceedings of the Sixth International Conference on Genetic Algorithms 1995; pp 136−143.
(39) Caruana, R. A.; Schaffer, J. D. Representation and hidden bias: Gray vs. binary coding for genetic algorithms. In Machine Learning Proceedings 1988; Elsevier, 1988, pp 153−161.
(40) Deng, H. W.; Zhang, C. B.; Xu, G. Q.; Tao, Z.; Zhang, B.; Liu, G. Z. Density measurements of endothermic hydrocarbon fuel at sub- and supercritical conditions. J. Chem. Eng. Data 2011, 56, 2980−2986.
(41) Deng, H. W.; Zhang, C. B.; Xu, G. Q.; Zhang, B.; Tao, Z.; Zhu, K. Viscosity measurements of endothermic hydrocarbon fuel from (298 to 788) K under supercritical pressure conditions. J. Chem. Eng. Data 2012, 57, 358−365.
(42) Deng, H. W.; Zhu, K.; Xu, G. Q.; Tao, Z.; Zhang, C. B.; Liu, G. Z. Isobaric specific heat capacity measurement for kerosene RP-3 in the near-critical and supercritical regions. J. Chem. Eng. Data 2012, 57, 263−268.
(43) Xu, G. Q.; Jia, Z. X.; Wen, J.; Deng, H. W.; Fu, Y. C. Thermal-Conductivity Measurements of Aviation Kerosene RP-3 from (285 to 513) K at Sub- and Supercritical Pressures. Int. J. Thermophys. 2015, 36, 620−632.

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